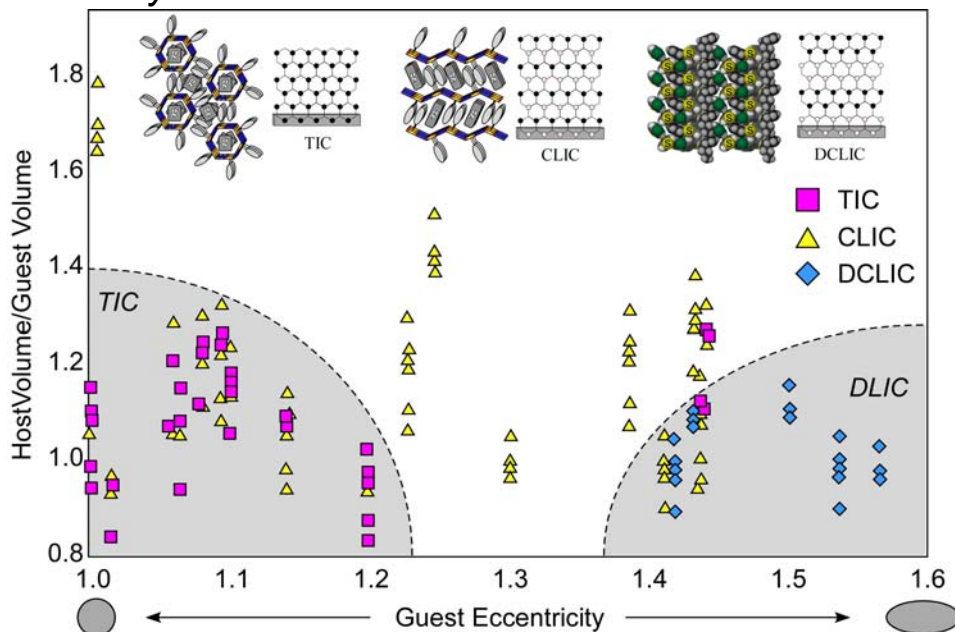
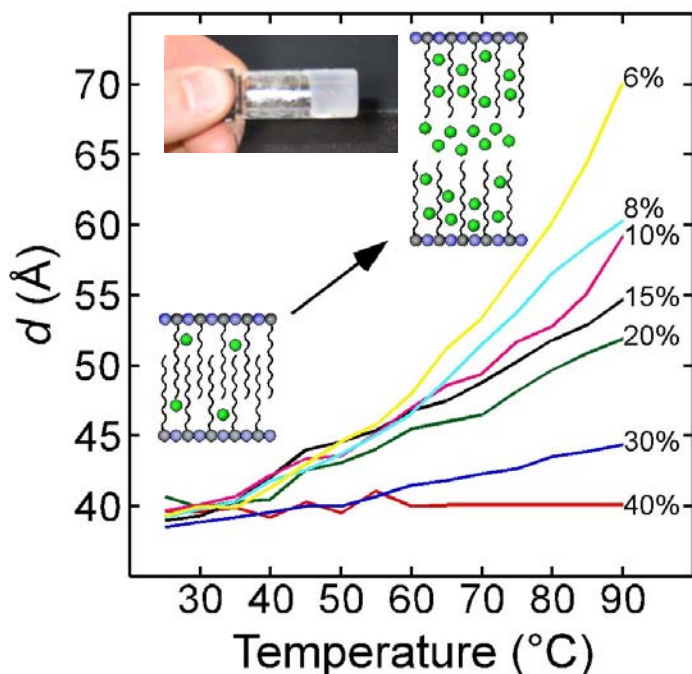


# Functional Organic Solid State Materials Derived from Designer Host Frameworks

DMR-0305278

Michael D. Ward, University of Minnesota

- Hydrogen-bonded organic lamellar structures behave like inorganic clays: A small amount of a crystalline compound comprising hydrogen-bonded sheets of guanidinium and sulfonate ions decorated with alkane chains dispersed in an organic solvent forms a gel that resists flow. X-ray scattering reveals that the gel contains layered structures swollen by the organic solvent. The layered structures swell to the extent that they are exfoliated, yet the 2-D hydrogen-bonded sheet is retained even though it is held together by non-covalent hydrogen bonding.



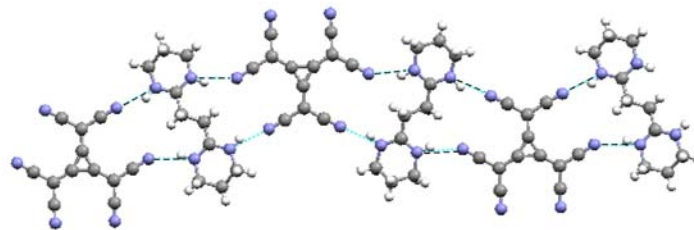
The selectivity for tubular and lamellar architectures in hydrogen-bonded host frameworks is dependent upon key molecular parameters such as the relative sizes of the host and guest molecules, which serve as templates that guide molecular assembly during crystallization, and the shape of the templates. These frameworks are based on the conformationally soft hydrogen-bonding guanidinium-sulfonate sheet, which can adopt a flat geometry in the CLIC and DCLIC frameworks or form nanoscale cylinders in the TIC frameworks. The organization of these architectures into distinct regimes on this diagram are helping us to develop structural concepts that may unite “soft solids” (crystals) with soft matter (lyotropic, thermotropic liquid crystals, block copolymers)

## Broader Impact Y2004

Michael D. Ward, University of Minnesota

### Education and Mentoring

- 3 Graduate students related to project: Matt Horner, Steve Martin, Sang-Jae Park
- 1 Postdoc: Sang-Ok Park
- 1 visiting KOSEF student (Seoul National University): Jinsoo Kim
- 1 visiting undergraduate performing summer research:  
Danielle Schacklady (guest student from Clemson/GaTech REU program sponsored by DMR). Danielle's work, soon to be submitted for publication, is the basis for collaboration established with Universite' Louis Pasteur (see below and accompanying graphic).



New hydrogen-bonded tape motifs serve as guides to possible porous crystalline networks

### Outreach

- Activities revolving around role as director of the University of Minnesota MRSEC (tribal college visits, overseeing overall operation of MRSEC-related outreach programs, including visiting faculty-student teams and individual undergraduates during summer 2003).

### Industrial connections

- Eli Lilly

### International and other Activities

- Associate Editor, Chemistry of Materials
- Director, University of Minnesota MRSEC
- Grazing incidence X-ray diffraction studies at the DESY synchrotron facility (Hamburg, Germany) with co-workers from the Weizmann Institute (*J. Am. Chem. Soc.* **2003**, 125, 15922): Demonstrated crystalline inclusion compounds at the air-water interface that are related to the 3-D crystalline host-guest materials developed in our laboratory with NSF support.
- Initiated collaboration with W. Hosseini, Universite' Louis Pasteur, Strasbourg, France examining new hydrogen-bonded solid state materials and epitaxial growth of isomorphous "core-shell" crystalline composites.
- Keynote lecturer at (a) RSC *Crystal Engineering Faraday Discussion 2004: New Trends in Crystal Engineering*, Nottingham UK; (b) Gordon Research Conference, Organic Structures and Properties, Les Diablerets, Switzerland; (c) COST D31: Organizing Non-Covalent Chemical Systems with Selected Functions, Academy of Sciences of the Czech Republic, Prague

# NOTES

The technical slide (page 1) describes two recent discoveries.

- Crystalline guanidinium alkylbenzenesulfonates have hydrogen-bonded guanidinium-sulfonate sheets separated by the long alkylbenzene groups. The alkyl chains are interdigitated. When small amounts of these compounds are added to water they form gels with rheological properties that suggest the presence of networks of wormlike micelles (an aqueous lyotropic phase) held together by the hydrogen bonding between the guanidinium and sulfonate ions. The panel at the left of page 1 illustrates the inverse example, an organic lyotropic phase that forms when these compounds are dispersed in organic solvents. In this case, the gels are lamellar (layered) in nature, and the gels form because the organic solvent is absorbed by the non-polar regions of the layers. Remarkably, the layers can be swollen by an amount that completely separates the alkane chains while retaining the lamellar structure (by X-ray) and the hydrogen-bonded sheet (by IR). This swelling behavior is very similar to behavior exhibited by inorganic clays, which often can be swollen with solvents after they have been exfoliated by surfactants, which bind to the surface of the clay sheets. In the case of clays, the inorganic sheets are held together by covalent bonds and the surfactant molecule chains bind to the sheet by non-covalent electrostatic interactions, but in our materials the sheet is held together by non-covalent hydrogen-bonding with the alkyl chains affixed to the sheet by covalent interactions. The rheological properties exhibited by guanidinium-sulfonate lyotropic nanostructures can impact several technologies (separations, drag reduction, personal care products, oil recovery). These materials also form smectic phases with very high viscosities that can be blended into polymers, with potential applications in gas barrier membranes.

- The second slide shows a very recent fundamental discovery. We previously found that the guanidinium organomonosulfonates could form host frameworks. Because the sheets are conformationally flexible, they could form lamellar crystalline architectures or they could curl into tubes. The diagram shown here illustrates that “round” guests prefer tubes while “oval” guests promote one of two lamellar phases. These lamellar phases are continuous in three dimensions due to interdigitation of the organic substituents projecting from the sheet (shown as filled and open circles, which represent up and down projections of the organic substituents from each sheet). This diagram represents an important advance in crystal design - correlating measurable molecular parameters with solid state structure so that prediction of crystal architecture is enabled. Combined with our observations of soft matter-like behavior for these compounds (lyotropic and thermotropic, see above), the formation of cylindrical and lamellar structural isomers is particularly intriguing, as related structures are also observed in lyotropic liquid crystals and block copolymers, even though these materials show organization at longer length scales.

